CXXXV.—*Oxidation of* p-*Aminophenyltrimethylammonium Methosulphate and Some Quaternary Ammonium Derivatives.*

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IT was proposed to compare the meta-directing power of the nitro- and the quaternary ammonium radical in one and the same nucleus by nitrating *p*-nitrophenyltrimethylammonium salts. It was, however, found impossible to synthesise the *p*-nitrophenyltrimethyl ammonium salt, a fact in itself not without significance. Methyl sulphate, very carefully purified, and *p*-nitrodimethylaniline interacted neither in benzene solution nor when heated under pressure. With methyl iodide, there was no reaction at 120° and carbonisation took place at 165°. *p*-Aminophenyltrimethylammonium chloride was then submitted to the oxidising action of Caro's salt, in the hope that the expected nitroso-derivative could be oxidised to the required nitro-compound. The product, however, proved to be the corresponding azoxy-compound :

$$2NH_2{\cdot}C_6H_4{\cdot}NMe_3Cl \longrightarrow ON_2(C_6H_4{\cdot}NMe_3Cl)_2$$

When this was nitrated, a nitro-group entered each nucleus in the ortho-position with respect to the azoxy-group.

Although comparison between the nitro- and the quaternary ammonium group could not be undertaken in the direct manner proposed, yet the superiority of the latter group over the former in its characteristic effects is plainly indicated by the failure to obtain the quaternary nitroso-compound required as compared with the fact that *p*-nitroaniline when similarly oxidised gives about an 80% yield of *p*-nitrosonitrobenzene. The first stage in the oxidation of an aniline by Caro's salt gives the corresponding phenylhydroxylamine (Bamberger and Tschirner, *Ber.*, 1899, **32**, 1675). A meta-directing group in the para-position would draw more or less heavily for electrons on the nuclear carbon atom carrying the hydroxylamino-radical, thereby increasing the conjugation of the tertiary nitrogen with the nucleus, at the same time decreasing its capacity for oxidation. The stronger the meta-directing group the less is the inclination of the hydroxylamino-nitrogen towards oxidation, and therefore the lower the state of oxidation of the final product. As an azoxy-compound represents a lower stage of oxidation than a nitroso-compound, the quaternary ammonium group must be more strongly meta-orienting than the nitro-group. A circumstance that gives strength to the ammonium radical in the present oxidation is that the reaction is carried out in aqueous solution and the salt is therefore almost completely ionised. Oxidation could not be carried out in other solvents.

The same effect underlies the unreactivity of *p*-nitrodimethylaniline towards methyl sulphate and methyl iodide. If this is the true explanation, one would expect less resistance in the ortho-compound and still less in the meta-compound. Accordingly experiments were carried out on *o*- and *m*-nitrodimethylaniline as well as on dimethylaniline itself. The last compound reacted vigorously with methyl sulphate in the cold in benzene solution, with the *m*-compound boiling was necessary, and no reaction occurred with the *o*-compound. The resistance of the *o*-compound to this addition is, however, limited, as it reacts with methyl iodide on heating under pressure (Friedländer and Dinesmann, *Monatsh.*, 1898, **19**, 636). The same order obtains for the solubility of these anilines in acids.

p-Dimethylaminobenzaldehyde, *p*-aldehydophenyltrimethylammonium methosulphate, and nitrosodimethylaniline condensed readily with diketohydrindene and with *p*-aminophenyltrimethylammonium chloride.

EXPERIMENTAL.

Action of Methyl Sulphate on Nitrosodimethylaniline.—The two substances reacted very slowly in benzene. In molecular proportion, without a solvent or in ethereal solution, they reacted vigorously. The dark red oily product was washed with ether and benzene and left in a vacuum over sulphuric acid for many weeks; it thickened considerably but failed to crystallise (Found: N, 9·9. $C_{10}H_{16}O_5N_2S$ requires N, 10·2%). In aqueous solution it gave barium sulphate on treatment with barium chloride, but no precipitate with perchloric or picric acid. Boiling alkali liberated a volatile base having the odour of dimethylamine. The compound would therefore appear to be the ψ-methosulphate corresponding to the ψ-methiodide prepared by Knorr (*Ber.*, 1897, **30**, 934).

p-*Acetamidophenyltrimethylammonium Methosulphate.*—To a boiling benzene solution of *p*-acetamidodimethylaniline (1 mol.) was added a benzene solution of methyl sulphate (1·5 mols.), with shaking. After 10 minutes' boiling, the mixture was cooled and the colourless crystals were collected, washed with benzene (yield, practically theoretical) and recrystallised from alcohol; the *methosulphate* then melted at 165° (Found: C, 47·2; H, 6·5. $C_{12}H_{20}O_5N_2S$ requires C, 47·4; H, 6·6%).

p-*Aminophenyltrimethylammonium Methosulphate.*—The preceding compound (1 g.) was heated on the water-bath with 10 c.c. of concentrated hydrochloric acid for 2½ hours: titration with standard sodium nitrite then showed that the hydrolysis was complete. Heating with concentrated sulphuric acid (2 c.c.) and water (3 c.c.) for 5 hours caused almost complete hydrolysis, but the use of smaller concentrations of the acid or heating for a shorter time resulted in incomplete hydrolysis.

p-Acetamidophenyltrimethylammonium methosulphate (3 g.) was hydrolysed with hydrochloric acid and then diazotised with sodium nitrite (0·68 g.) at 0°. The cold solution was neutralised with sodium carbonate and mixed with α-naphthol (1·44 g.) dissolved in an equivalent of aqueous sodium carbonate. After a few hours, addition of perchloric acid to the crimson solution precipitated p-*α-naphtholazophenyltrimethylammonium perchlorate,* which crystallised from 90% alcohol in red needles, m. p. 247° (decomp.) (Found : N, 10·3. $C_{19}H_{20}O_5N_3Cl$ requires N, 10·3%).

The *perchlorate* of the β-naphthol compound, similarly prepared, had m. p. 267° (decomp.) (Found : N, 10·1%).

A similarly diazotised solution was treated with α-naphthylamine in dilute hydrochloric acid. p-*α-Aminonaphthaleneazophenyltrimethylammonium chloride,* which was slowly precipitated, crystallised from alcohol–dilute hydrochloric acid in long reddish-violet needles, m. p. 196° (decomp.) (Found : N, 14·5. $C_{19}H_{21}N_4Cl,HCl$ requires N, 14·8%).

p-*Dimethylaminobenzeneazophenyltrimethylammonium Perchlorate.*—Molecular quantities of nitrosodimethylaniline and *p*-aminophenyltrimethylammonium chloride were boiled together in hydrochloric acid solution and perchloric acid was then added. The long brown needles of the *perchlorate* that had formed after 24 hours were recrystallised from dilute perchloric acid solution. They charred above 280° (Found : N, 11·4. $C_{17}H_{23}O_4N_4Cl,HClO_4$ requires N, 11·6%).

p-*Dimethylaminobenzylidene*-p-*aminophenyltrimethylammonium Perchlorate.*—When *p*-dimethylaminobenzaldehyde (1 mol.) and *p*-aminophenyltrimethylammonium chloride (1 mol.), each in hydrochloric acid solution, were mixed, a greenish-yellow colour developed at once, indicating that the condensation in this case takes place at the ordinary temperature. The mixture was boiled to complete the reaction, concentrated, and perchloric acid added. The copious precipitate obtained crystallised from dilute perchloric acid solution in orange-red needles, m. p. 253° (decomp.) (Found : N, 8·6. $C_{18}H_{24}O_4N_3Cl,HClO_4$ requires N, 8·7%).

Oxidation of p-*Aminophenyltrimethylammonium Chloride.*—The solution in hydrochloric acid obtained by hydrolysis of the acetyl compound (see p. 1079) was neutralised with aqueous sodium hydroxide, cooled with ice, and treated with the equivalent amount of ammonium persulphate made into Caro's salt by Willstätter's method (*Ber.*, 1909, **42**, 1842). The deep brownish-red solution of azoxybenzene-*pp'*-bistrimethylammonium chloride produced was kept for several hours and the following three salts were then prepared from it.

(1) The *perchlorate*, $ON_2(C_6H_4{\cdot}NMe_3{\cdot}ClO_4)_2$, precipitated by the addition of perchloric acid to the neutral or slightly alkaline solution, crystallised from a mixture of dilute aqueous perchloric acid and alcohol in needles which varied in colour from yellow to brown and red. It melted and decomposed at 268°, sometimes with violent explosion (this property made the estimation of carbon and hydrogen impossible) (Found: N, 10·7, 10·6, 10·8; Cl, 13·7. $C_{18}H_{26}O_9N_4Cl_2$ requires N, 10·9; Cl, 13·8%), and was identical with the synthetic perchlorate described on p. 1084.

(2) The *picrate*, precipitated from the neutral solution of the salt with aqueous picric acid, crystallised from much acetone and water (10 : 8) after several hours in needles, m. p. 244° (decomp.). It was analysed after several crystallisations. Notwithstanding its explosiveness, determinations of carbon and hydrogen were successful twice, a large excess of copper oxide and a very long copper spiral being used (Found: C, 46·9, 46·7; H, 4·2, 4·2; N, 18·0. $C_{30}H_{30}O_{15}N_{10}$ requires C, 46·7; H, 4·2; N, 18·2%).

(3) The ferricyanide was obtained by the addition of a solution of potassium ferricyanide. This salt is a very sparingly soluble, uncrystallisable, greenish-yellow substance. When it is boiled with a slight excess of copper sulphate solution, and the filtered liquid is freed from copper and sulphate ions by baryta, and then from barium by passage of carbon dioxide, the final filtrate contains the quaternary carbonate, from which other salts can be obtained by neutralising the solution with the requisite acid.

The chloride was obtained by boiling the picrate with a large excess of concentrated hydrochloric acid. After cooling, the picric acid was removed by filtration and by repeated extraction with ether, and the filtrate evaporated to dryness on the water-bath. The deep red, glassy residue, which was extremely deliquescent, was crystallised from much absolute alcohol and dried in a vacuum desiccator. The straw-coloured needles of the chloride quickly reddened in the air. The highest melting point observed was 252° (decomp., preceded by considerable shrinkage).

The iodide was precipitated when solutions of the chloride and of sodium iodide in alcohol were mixed and was recrystallised from much methyl alcohol and dried in a vacuum desiccator; the orange plates obtained melted at 198° (decomp.). In the air the iodide absorbed moisture and turned brown.

Volumetric Analysis of Azoxybenzene-pp′-*bistrimethylammonium Perchlorate.*—This application of Knecht and Hibbert's titanous chloride method (" New Reduction Methods in Volumetric Analysis," 1925) to the estimation of the azoxy-group is novel. Through a mixture of 0·0300 g. of the perchlorate, 100 c.c. of water, and 10 c.c. of concentrated hydrochloric acid, carbon dioxide was passed for 10 minutes. The solution was then warmed to 60—70° and titrated with standard titanous chloride until the yellow colour was destroyed. Towards the end of the titration, at least 3 minutes were allowed after the addition of every 0·5 c.c. of the chloride, as the reduction was then by no means instantaneous. The end-point was not very sharp (Titres found : 26·2, 26·4, 26·0, 27·2 c.c. Calc. : 25·8 c.c.). The presence of the perchlorate ion has no effect on the titanous chloride at the dilution used, as was proved by blank experiments on potassium chlorate solutions. The indirect method (excess of titanous chloride and back-titration) was useless.

Nitration of Azoxybenzene-pp′-*bistrimethylammonium Salts.*—Nitric acid alone had no nitrating action on the azoxy-chloride; when the solution was evaporated to dryness, the *nitrate* remained. This crystallised from anhydrous methyl alcohol in small, light orange, needle-like prisms, m. p. 220—222° (decomp.). It was hygroscopic, but was practically insoluble in absolute alcohol and acetone (Found : N, 18·8. $C_{18}H_{26}O_7N_6$ requires N, 19·2%).

When the nitrate (1·5 g.) was added to concentrated nitric acid (10 c.c.; *d* 1·42), followed by concentrated sulphuric acid (15 c.c.), a vigorous action took place with evolution of oxides of nitrogen in the cold. The solution was boiled for 1·5 hours, the resulting clear yellow liquid diluted and neutralised with sodium carbonate, and perchloric acid added. The *dinitroazoxybenzene*-pp′-*bistrimethylammonium perchlorate* obtained crystallised from aqueous alcohol in deep brown crystals, m. p. 265° (decomp.) {Found : N, 13·9. $ON_2[C_6H_3(NO_2)\cdot NMe_3\cdot ClO_4]_2$ requires N, 14·0%}. The corresponding *chloride*, obtained from the picrate by treatment with concentrated hydrochloric acid as previously described, crystallised from dilute hydrochloric acid in thin, reddish-brown, rectangular plates which melted with decomposition (Found : N, 17·3. $C_{18}H_{24}O_5N_6Cl_2$ requires N, 17·7%).

The diamine produced by complete reduction of the nitro-compound with zinc and hydrochloric acid was an *o*-diamine, for it gave a deep wine colour with ferric chloride and condensed instantly with phenanthraquinone on the addition of a drop of alkali, giving a dark green precipitate.

Diketohydrindene Condensations.—These were undertaken with the object of comparing the reactivities of the nitroso- and the aldehydo-group and of studying the effect on the reactivity of a quaternary ammonium group in the para-position.

With nitrosodimethylaniline. Molecular quantities of diketohydrindene and nitrosodimethylaniline were boiled together in absolute alcohol for 3 minutes. At once, a deep blood-red colour developed and a crystalline *compound* separated; this, after being washed with absolute alcohol and dried, melted at 210° (decomp.) (Found: N, 9·8. $C_{17}H_{14}O_2N_2$ requires N, 10·1%).

With p-*dimethylaminobenzaldehyde.* The condensation was carried out as in the last experiment and took place just as quickly. The product separated from alcohol in crystals with a blue lustre, m. p. 99—100° (compare Noelting and Blum, *Ber.*, 1901, **34**, 2467).

With p-*aldehydophenyltrimethylammonium methosulphate.* Equimolecular quantities of the methosulphate (see below) and diketohydrindene were boiled in absolute alcohol. The colour changed from yellow to orange and the reaction was complete in less than 5 minutes. Water was then added and the solution was extracted with benzene to remove any excess of diketohydrindene and boiled. On standing, the *product* separated in deep orange needles, which were washed with a little alcohol and dried; m. p. 243° (decomp.) (Found: N, 3·5. $C_{20}H_{21}O_6NS$ requires N, 3·5%).

With the azoxy-quaternary salts. These were recovered unaltered when a similar condensation was tried with them.

p-*Aldehydophenyltrimethylammonium Methosulphate.*—Pure dry methyl sulphate was mixed in slight excess with *p*-dimethylaminobenzaldehyde and warmed very gently to start the reaction, which proceeded rather violently. The voluminous frothy product, on cooling, changed to a small, dark red, glassy mass which became crystalline in a few hours. The *methosulphate,* recrystallised from hot methyl alcohol, formed long yellow needles, which were washed with ether dried over sodium. They were extremely soluble in water and melted at 138—139° (Found: N, 5·2; OMe, nil. $C_{11}H_{17}O_5NS$ requires N, 5·1%).

The *perchlorate* was precipitated from a solution of the methosulphate as an oil which slowly solidified. It crystallised from dilute perchloric acid solution after some time in yellow plates, m. p. 140—141° after being washed with absolute alcohol and dried. It was appreciably soluble in water and puffed strongly when heated in a flame (Found: N, 5·4. $C_{10}H_{14}O_5NCl$ requires N, 5·3%).

Benzylideneaniline-pp′-*bistrimethylammonium Perchlorate.*—*p*-Aminophenyltrimethylammonium chloride in hydrochloric acid solution was boiled with an equivalent quantity of *p*-aldehydophenyltrimethylammonium methosulphate and perchloric acid was then added; after 2 days, long, thin, slightly yellow needles had formed. These when dry became deep red at 240° and charred at about 260°. Heated in a flame, the compound exploded (Found : N, 8·2. $C_{19}H_{27}O_8N_3Cl_2$ requires N, 8·4%).

Addition of Methyl Sulphate to pp′-*Tetramethyldiaminoazoxybenzene.*—Methyl sulphate (1½ mols.) was added to the base (1 mol.), and enough benzene to ensure its solution on boiling, which was continued under reflux for an hour. The benzene was then decanted, the product washed with ether, and the coffee-brown crystalline residue dissolved in water. Addition of perchloric acid precipitated a perchlorate which, after being crystallised from alcohol–dilute perchloric acid solution and dried, melted, alone or mixed with the azoxy-perchlorate described on p. 1081, at 268° (decomp.). The two picrates also were identical.

m-*Nitrophenyltrimethylammonium Methosulphate.*—A mixture of *m*-nitrodimethylaniline (28 g.; 1 mol.), methyl sulphate (30 g.; 1·5 mols.), and benzene (25 c.c.) was heated in a water-bath for 1 hour. The heavy oil produced solidified on cooling, and after decantation of the benzene and washing with ether the residue crystallised from slightly aqueous alcohol in thin needle-like plates, m. p. 220°, which were very soluble in water (Found : N, 9·5. $C_{10}H_{16}O_6N_2S$ requires N, 9·6%).

The *picrate* crystallised from water in yellow prismatic plates, m. p. 150° (decomp.) (Found : N, 17·1. $C_{15}H_{15}O_9N_5$ requires N, 17·1%), and the *perchlorate* from dilute perchloric acid solution in white feathery needles, m. p. 230—232° (decomp.) (Found : N, 9·9. $C_9H_{13}O_6N_2Cl$ requires N, 10·0%).

The *iodide*, obtained by adding a concentrated solution of sodium iodide to a solution of the methosulphate, crystallised from water in large white needles, m. p. 202° (Found : N, 8·9. $C_9H_{13}O_2N_2I$ requires N, 9·1%).

Phenyltrimethylammonium Methosulphate.—When a solution of dimethylaniline (30 g.; 1 mol.) in benzene (20 c.c.) was treated with methyl sulphate (30 g.; 1 mol.), it soon got hot and the benzene boiled away even through a reflux condenser. The oily product quickly solidified and then crystallised from acetone in colourless needles. The *perchlorate*, precipitated with perchloric acid from a solution of the methosulphate, crystallised from dilute perchloric acid solution in colourless needles (Found : N, 5·8. $C_9H_{14}O_4NCl$ requires N, 5·9%).

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